

CERTIFICATE OF EXPRESS MAILING

I HEREBY CERTIFY that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated below, in an envelope addressed to the Commissioner of Patents and Trademarks, Washington, DC 20231.

DATE OF DEPOSIT: Feb. 4, 1997

EXPRESS MAIL LABEL NO: EM057349120US

Margaret M. Dunbar

Signature

Margaret M. Dunbar

Printed Name

PATENT APPLICATION
DOCKET NO. MICR154 (95-0392)

DOCKETED

Method For In-situ Cleaning of Inductively-Coupled Plasma Chambers

INVENTORS:

Gurtej S. Sandhu

Sujit Sharan

AI Device

Method For In-situ Cleaning of Inductively-Coupled Plasma Chambers

Two > A'

DESCRIPTION

BACKGROUND OF THE INVENTION

5

Technical Field. This invention relates to integrated circuit manufacturing processes and, more specifically, to a novel process for plasma fabrication procedures for semiconductor substrates using conductive materials.

Background. In order to build an integrated circuit, many active devices
10 need to be fabricated on a single substrate. The current practice in semiconductor manufacturing is to use thin film fabrication techniques. A large variety of materials can be deposited using thin films, including metals, semiconductors, insulators and the like. The composition and uniformity of these thin layers must be strictly controlled to facilitate etching of submicron features. The surface of the substrate, most often a wafer,
15 must be planarized in some way to prevent the surface topography from becoming increasingly rough with each added thin film level. The formation of such films is accomplished by a large variety of techniques.

Chemical vapor deposition (CVD) processes are often selected over competing deposition techniques because they offer numerous advantages, including the abilities of
20 CVD to deposit films from a wide variety of chemical compositions and provide improved conformality.

In general a CVD process includes the following steps: a selected composition and flow rate of reactant and inert gases are dispatched into a reaction chamber; the gases move to the substrate surface; the reactants are adsorbed on the substrate surface; the
25 species undergo a film-forming chemical reaction and the by-products of the reaction are desorbed from the surface and conveyed away from the surface.

Plasma enhanced CVD (PECVD) uses a plasma or glow discharge with a low pressure gas, to create free electrons which transfer energy into the reactant gases. This allows the substrate to remain at a lower temperature than in other CVD processes. A
30 lower substrate temperature is the major advantage of PECVD and provides film

deposition methods for substrates that do not have the thermal stability necessary for other processes that require higher temperature conditions. In addition, PECVD can enhance the deposition rate when compared to thermal reactions alone, and produce films of unique compositions and properties.

5 In most applications it is desired that thin films maintain a uniform thickness and freedom from cracks or voids. As thin films cross steps that occur on the surface of the underlying substrate, they often suffer unwanted deviations from the ideal conformality, such as thinning or cracking. A measure of how well a film maintains its nominal thickness is referred to as the step coverage of the film. The height of the step and the
10 aspect-ratio (the height-to-spacing ratio of two adjacent steps) of a feature being covered determine the expected step coverage. Step coverage of 100% is ideal, but normally a value less than 100% is specified as acceptable, for any given application.

 The semiconductor industry's continuing drive towards closer and smaller device geometries, has placed an increased demand for cost-effective solutions for the problem
15 of higher step coverage and planarization. New plasma sources are being developed because traditional sources cannot extend to the sub-0.5 micron level of processing necessary for the more rigorous device geometries. Fabrication processes that are employed in response to the necessity of good conformality in the face of the submicron geometries include plasma enhanced directional sputtering, plasma enhanced etching and
20 plasma enhanced chemical vapor deposition. CVD processes have been developed for some metals, for example titanium and titanium nitride, both of which can be put to use in 0.35 and 0.25 micron devices. Because these typical back-end-of-the-line (BEOL) fabrication processes must be done at low temperatures (<450° C) to protect the integrity of previously deposited layers and to ensure that dopants don't diffuse excessively, they
25 are typically based on PECVD, which, as described above, can be achieved at low temperatures. These low temperature, high aspect ratio coverage PECVD process requirements are being met with low pressure, high density plasma (HDP) based processes. To achieve the good step coverage and gap fill desired, HDP CVD systems are run at a high flow rate to achieve adequate deposition. At the same time HDP CVD

process pressures need to be relatively low for the plasma to operate properly -- that is at high densities.

To deposit or etch conductive or metal films using HDP processes, the plasma must necessarily be generated using inductive coupling. The fabrication by deposition or removal of metal thin films in an inductively coupled high density plasma reactor is desirable because of the advantages it provides, including: lower processing temperatures and higher step coverage, as discussed above, as well as shorter processing times and denser films.

However, in the case of inductively coupled (IC) plasma procedures there is no capacitive coupling to the chamber walls, and any conductive material deposition on the chamber walls blocks the inductive power coupling to the plasma. For the deposition of conductive materials and metal films this means that the reactor chamber walls must be cleaned quite frequently in order to prevent the deposition of conductive materials on the chamber walls which blocks the IC plasma fabrication steps.

Traditionally the only way to remove ionic and metallic contaminants from any plasma reaction chamber or furnace tube has been to clean the tubes with wet etching, often with the simple method of manually rolling them, half submerged, in an acid bath. Cleaning of the reaction chamber in this manner involves removing the dirty quartz tube, installing a previously cleaned tube, and cleaning the dirty tube for future use. This method of cleaning is unsatisfactory for many reasons. Tearing down a furnace is a time consuming and difficult process that requires from 4-24 hours and has been likened to "open heart surgery". It requires not merely a tube change, but also a particle and process requalification of the furnace. The result is that any cleaning regime selected must balance the need to clean the furnace tube with the potential product yield loss and furnace downtime. In addition, a very significant disadvantage of any wet clean process is the increasingly strict regulatory controls placed on wet chemical disposal making it increasingly more costly and troublesome.

Several *in-situ* cleaning options exist for other CVD systems but metal and other conductive material contamination cannot be removed completely with any of the existing methods. Any conductive deposition on the chamber walls in an IC plasma

system blocks the power coupling to the plasma. The significance of this is that in the specific case of inductively coupled plasma chambers, since there is no capacitive coupling to the chamber walls, cleaning by generating a plasma containing an etchant gas to remove conductive material is not possible. With the growing need for more frequent
5 cleaning of furnace tubes, as is the case when using IC PECVD to deposit metals and conductive films an alternative cleaning method is still needed.

SUMMARY OF THE INVENTION

The present invention is a process for plasma enhanced fabrication of conductive
10 materials on a semiconductor substrate comprising the steps of placing the substrate in an inductively coupled (IC) plasma reaction chamber and maintaining the chamber under vacuum pressure while introducing at least a preselected reactant species gas, and optionally a carrier gas into the chamber for a preselected fabrication procedure on the substrate. A plasma is generated from the gas or gases within the chamber using a power
15 source inductively coupled to the reaction chamber. After the consequent fabrication procedure the substrate is removed from the chamber; and any conductive material is *in-situ* removed from the inside of the chamber to remove any blocking of the inductive power couple to the reaction chamber.

In one embodiment the *in-situ* removal of conductive material from the inside of
20 the reaction chamber is accomplished by the introduction of a remotely created plasma, which provides the necessary activated reactive species to carry out this step. The activated reactive species are created in a separate plasma reaction chamber, which is remote and separate from the inductively coupled PECVD chamber and then transported downstream and introduced into the reaction chamber to remove conductive material
25 from the inside of the reaction chamber.

In another embodiment the *in-situ* removal of conductive material is accomplished employing low temperature etching by the introduction of suitable etchant gases into the chamber. Suitable gases for etching the conductive materials, such as metals, contained in the fabrication step include, for example, compounds such as ClF_3 ,
30 other polyhalogen compounds or NF_3 .

Additional advantages and novel features of the invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention.

5

add > #2

DESCRIPTION OF THE FIGURES

Figure 1 is a schematic drawing of an exemplary inductively coupled plasma-enhanced chemical vapor deposition chamber suitable for use with the process of this invention.

10 Figure 2 is a flow chart of the steps for the given embodiment of the process of this invention.

DETAILED DESCRIPTION

15 The present invention, broadly stated, is directed to plasma enhanced fabrication processes. The invented process permits the *in-situ* removal of conductive material from the inside of an inductively coupled plasma chamber. In general, for any fabrication procedure or step that utilizes a plasma or glow discharge in an inductively coupled reaction chamber and involves a conductive material, the selected fabrication step may be completed and followed by *in-situ* removal of conductive material from the inside of the inductively coupled plasma reaction chamber. Because of the nature of glow discharges
20 or plasmas and conductive material, for example metals, such plasma enhanced processes must necessarily be carried out in an inductively coupled (IC) reaction chamber. The invention is particularly well-suited to processes that use metal-containing compounds and/or high density plasmas.

25 A plasma enhanced chemical vapor deposition (PECVD) process is described in detail to illustrate the utility of the process. The process is equally suited to any other process that uses a plasma in an inductively coupled reaction chamber and a conductive material. The exemplary embodiment using PECVD is not intended to limit the scope of the present invention to PECVD processes. Other appropriate processes for the present invention include, for example, plasma enhanced directional sputtering, etching of metals
30 with high density plasma, surface conditioning treatments, and the like.

For PECVD metal film deposition in an IC chemical vapor deposition (CVD) reactor, the process of the invention, generally stated, includes the steps of: placing the substrate in a IC CVD reaction chamber under a preselected vacuum pressure; introducing a preselected composition of processing gas into the reaction chamber for metal deposition on the substrate; and generating a high density plasma from the gas within the reaction chamber using a power source inductively coupled to the reaction chamber; removing the substrate from the reaction chamber; and *in-situ* removal of conductive films from the inside of the chamber, to remove blocking of the inductive power couple to the reaction chamber. The *in-situ* chamber cleaning is accomplished by either introduction of activated reactive compounds , preferably contained in a remotely formed plasma for etching conductive materials or by introduction of gases for etching conductive materials.

The *in-situ* chamber cleaning process can be performed in any system for inductively coupled (IC) plasma enhanced (PE) fabrication processes. An IC high density plasma (HDP) system is described below and shown in FIG. 1 and is generally designated as 10. It is to be understood that the apparatus and embodiments described herein are meant to be a non-limiting examples to illustrate the process claimed in this invention.

A radio-frequency inductively coupled type of PECVD apparatus is provided with: a reaction chamber 12 that has a gas inlet port 14 in flow communication with a source, which is not shown, for supplying a metal precursor deposition gas 30 and a gas exhaust port 16 in flow communication with a source of vacuum for exhausting gas from chamber 12 and for maintaining a predetermined degree of vacuum therein. System 10 further includes a plasma generation means 22 arranged on an upper surface of reaction chamber 12; and a holder device 18 that holds a substrate 20, typically a semiconductor wafer, on which the metal deposition process step is performed in the plasma produced by the plasma generation means 22. Reaction chamber 12 is formed from an insulating material that is transparent to radio-frequency waves, for example quartz.

Plasma generation means 22 in this example includes a radio-frequency power source to three-turn antenna 26. Radio-frequency waves are generated inside reaction

chamber 12 from antenna 26, and metal precursor deposition gas 30 is activated by this electromagnetic energy to cause the generation of a plasma.

Optionally, as shown in figure 1, is a common configuration for holder device 18; here a susceptor, such that another radio-frequency power source 24 is connected thereto with a matching circuit 28 therebetween; radio-frequency electric power is supplied from this radio-frequency power source, and a self-bias potential is maintained with respect to the plasma's potential, via a blocking capacitor (not shown).

A source of conductive material, here metal precursor deposition gas 30, can be appropriately coupled to inlet port 14, through which deposition gas 30 is introduced into chamber 12. Optionally, a supply of carrier gas 32 can be added to metal precursor deposition gas 30 by inclusion of a suitable gas premix system that is likewise coupled to enter chamber 12 through suitable valving. Carrier gas 32 may include argon, helium and other suitable inert gases. With this arrangement inert carrier gas 32 and metal precursor deposition gas 30 can be combined prior to introduction into reaction chamber 12. The temperatures and flow rates of the gases can be controlled to achieve the desired reaction and film quality.

The flow rates of metal precursor deposition gas 30 and carrier gas 32 also have a significant effect on the deposited film. For a IC HDP reactor 10, as described above process temperatures in the range of 200° C. to 800° C. can be utilized. Process pressures for such an IC HDP reactor 10 may be in the range of 1 m Torr to 10 m Torr and with gas flow rates in the range of 100 to 800 sccm's (standard cubic centimeters per minute).

Power from radio-frequency power source 22, typically is in the range of 50 to 150 watts with a frequency of the order of 13.56 MHz. Radio-frequency waves are generated with reaction chamber 12 from antenna 26. This electromagnetic energy excites deposition gas 30 and optionally carrier gas 32, now resident in chamber 12 to form a plasma, and thus a high-density plasma of, for example, the order of 10^{10} to 10^{16} ions/cm³ is generated.

An example of a metal film that can be deposited using this process is titanium. In the deposition of a titanium metal film using this invention a desirable precursor deposition gas can be formed from titanium tetrachloride (TiCl₄). Argon can be used as a

carrier gas and bubbled through the TiCl_4 to form the gas. Alternatively, a precursor deposition gas for titanium may be selected from any suitable titanium source, including for example, titanium tetrabromide, titanium tetraiodide, tetrakis (diethylamino) titanium and ~~tetrakis~~^{tetrakis} (diethylamino) titanium.

5 The method of the invention is equally suitable for the deposition, conditioning, doping and etching of other metal and conductive films and suitable precursors for the selected fabrication reaction can be formed from an organic or inorganic metal source, as dictated by the characteristics desired in the selected fabrication step. In the titanium deposition example, substrate 20 is placed on holder 18 inside reaction chamber 12 and
10 vacuum pressure is established by a vacuum pump, not shown, that is in flow communication with exhaust port 16. The TiCl_4 , hydrogen and argon gas are then introduced into reaction chamber 12 through inlet port 14. A plasma is generated by application of radio-frequency power source 22, as described above and a metal film is formed on the surface of substrate 20. Substrate 20 is then removed from reaction
15 chamber 12 and any deposition of metal on the inside of reaction chamber 12 can then be removed *in-situ* to eliminate any blocking of the inductive power couple to reaction chamber 12. Chamber 12 is then ready for another substrate 20 for the selected fabrication procedure, here metal deposition.

In one illustrative embodiment the *in-situ* removal of conductive material from the
20 inside of reaction chamber 12 is accomplished by the introduction of a remotely created plasma, which provides the necessary activated reactive species to carry out this step. Here reactive species includes ionized species and neutral species in high energy states. To accomplish this, the reactive species are created in separate plasma reaction chamber 40, which is remote and separate from inductively coupled PECVD chamber 12 and then
25 transported downstream and introduced into reaction chamber 12 to etch conductive material from the inside of chamber 12. This requires remote plasma chamber 40 to be in flow communication by way of inlet port 14 with reaction chamber 12. In the present example, the plasma for *in-situ* cleaning is generated in remote plasma chamber 40 and moved to reaction chamber 12 through conduit 13 to inlet port 14. The plasma
30 containing the reactive etchant species can be generated in remote plasma chamber 40, by

any suitable means to create the reactive species necessary for the *in-situ* cleaning step of the invention. Means for generating such a plasma are well known in the art and include, for example, a pair of oppositely placed electrodes, inductive coils, microwave sources, and other conductive and inductive power sources. In this example a plasma is the preferred means for creating the activated reactant species, but they can also be created using other suitable means, such as optical activation, thermal activation, ultrasonic activation and the like.

In another illustrative embodiment the *in-situ* removal of conductive material from the inside of reaction chamber 12 is accomplished employing low temperature etching by the introduction of suitable etchant gases into chamber 12 through inlet port 14. Suitable gases for etching the metals contained in the metal deposition step include, for example, compounds such as ClF_3 , other polyhalogen compounds or NF_3 . Additional examples of compounds suitable for etching the metals contained in the metal deposition step are listed elsewhere in this description.

In any embodiment the *in-situ* removal of conductive material from the inside of reaction chamber 12 is accomplished in the same manner after the preselected fabrication procedure. Whether the selected fabrication procedure is sputtering, etching or otherwise conditioning substrate 20, the selected fabrication step is then followed by *in-situ* cleaning of reaction chamber 12. For any preselected fabrication procedure the *in-situ* removal of conductive material from the inside surface of inductively coupled chamber 12 is accomplished by either introduction of a remotely formed plasma containing reactive compounds for etching conductive materials or by introduction of gases for etching conductive materials.

In any embodiment of the invention, after the *in-situ* removal of the conductive material from the inside of reaction chamber 12 has been accomplished, the etchant-containing species can then be pumped out of reaction chamber 12 through exhaust port 16. Likewise, in any embodiment the *in-situ* cleaning step may be considered to be performed as either a first step or last step in the metal deposition process claimed herein, as shown in Figure 2.

Turning now to the etchant gas sources for the *in-situ* cleaning step in any embodiment of the inventive process, they can be provided in any form that produces the desirable reactive species relative to the metal or conductive material that needs to be removed from the inside of chamber 12 in order to remove any blocking of the inductive power couple to reaction chamber 12. Typical examples of suitable etchant compounds include fluorine, chlorine, bromine, hydrogen chloride, hydrogen fluoride, hydrogen bromide, sulphur hexafluoride, nitrogen trifluoride, carbon tetrachloride (CCl₄), carbon tetrafluoride (CF₄), chlorine monofluoride (ClF), chlorine trifluoride (ClF₃), bromine chloride (BrCl), bromine monofluoride (BrF), bromine trifluoride (BrF₃), bromine pentafluoride (BrF₅), iodine monobromide (IBr), iodine tribromide (IBr₃), iodine monochloride (ICl; alpha and beta), iodine trichloride (ICl₃), iodine pentafluoride (IF₅), iodine heptafluoride (IF₇), carbon dichlorodifluoride (CCl₂F₂), other halogen and polyhalogen compounds and the like. The etchant source gases can be provided in either a gas phase or as liquid source converted to the gas phase through a bubbler system.

In conclusion, this plasma enhanced method for fabrication procedures that involve conductive material, using an inductively coupled plasma chamber with *in-situ* cleaning of the reaction chamber provides many advantages. These advantages include, for example, improved film condition and quality, in terms of step coverage, film density and multi-layer integrity. This invention provides a method for fabrication procedures for semiconductor substrates involving conductive material and employing a plasma for the smaller geometries that are now crucial to device functionality. This invention allows inductively coupled plasma chambers to be cleaned without dismantling, re-assembling and recertifying the plasma chambers. ^{AY} Other examples of the advantages provided by this invention include higher system throughput and reduced chemical disposal costs and other economic benefits.

It is intended that alternate embodiments of the inventive concepts are possible without departing from the scope of the invention as expressed in the following claims.